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Effect of Post-Annealing on the Properties of Eu Doped ZnO Nano Thin Films

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Abstract

Europium (Eu) doped nanostructure ZnO thin films are prepared by using spray pyrolysis technique. The ZnO:Eu thin films are deposited at a substrate temperature of 623 K on glass substrates, using europium nitrate as a Eu source. The as-prepared ZnO:Eu films are annealed in air at 673 K and 723 K for 1 h. The effect of post-annealing on the structural, electrical and optical properties of the films has been studied. XRD measurements show that all the films are nanocrystallized in the hexagonal wurtzite structure and exhibit a preferential orientation along (002) plane, the intensity of preferentially oriented (002) peak is apparently improved. The resistivity of annealed film is larger than the as-deposited. ZnO:Eu film annealing at 723 K for 60 min exhibits lowest resistivity of $3.62 \times 10^{-4} \Omega \text{ cm}$. In addition, the ZnO:Eu film shows good optical transmittance of 94%.

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Keywords: Spray pyrolysis, ZnO, Structural properties, SEM-EDX, Optical properties, Electrical conductivity

1. Introduction

Due to their optical and electrical properties metal oxide semiconductor films have been widely studied and have received considerable attention in recent years. Some of them are good candidates for transparent conductive films, if they are prepared off-stoichiometry or doped with suitable impurities. Such films have applications in electronic and optoelectronic devices photothermal and photovoltaic conversion, etc.

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ZnO is one of the metal oxide semiconductors suitable for use in optoelectronic devices, as an alternative material to tin oxide and indium tin oxide. ZnO is one of the metal oxide (II-VI group) semiconductors suitable for use in optoelectronic devices, as an alter-native material to tin oxide and indium tin oxide (Hirschwald, 1981). Its exceptional luminescent properties in ultraviolet (UV) and visible region have been studied by many groups (Ishizumiet al., 1999). Besides this, ZnO as a very attractive host lattice for doping of several luminescence centers. Generally, the II-VI group semiconductors doped with luminescence centers exhibit efficient luminescence even at room temperature. The luminescence of ZnO:Eu films was observed due to energy transfer from ZnO host to the Eu^{+3} ion in highly oriented c-axis ZnO films (Che et al., 2007). Moreover, rare-earth complexes have the ability to absorb light at shorter wavelength and emit at a longer wavelength. Luminescent rare earth nano-materials are very important in developing new display devices for various applications. The physical properties such as band gap and luminescence properties of the nano-sized rare earth compounds depend on the shape and size (Ariga et al., 2008; Wang et al., 2007; Jia et al., 2001; Nissamudeen et al., 2010). Rare earth (RE) doped semiconductors have been intensively studied for their potential use in optoelectronic devices like visible (blue, green, and red) and infrared luminescent devices (Cheng et al., 2005; Abdullah et al., 2003; Lima et al., 2003). Among the rare earth elements, europium (Eu^{3+}) was one of the trivalent rare earth ions which have been doped in ZnO to achieve efficient luminescent properties and at same time maintain high optical transparency.

A variety of methods has been used to grow rare earth (RE) doped zinc oxide thin films including chemical vapor deposition, sol–gel, magnetron sputtering, and evaporation (Takahiro et al., 2012; Wang et al., 2001; Shinho, 2013). In this study, authors concentrate on the structural, compositional, morphological, electrical transport and optical properties of Eu doped ZnO films deposited by spray pyrolysis technique. The spray pyrolysis technique was credited with several advantages, such as deposition of high purity, homogeneous, cheaper, large area films at relatively low temperatures.

The crystalline structure was analyzed by X-ray diffractometer (XRD, Rigaku,D/Max ULTIMA III, Japan). The surface morphology and elemental analysis were investigated using scanning electron microscope (SEM, Hitachi-S3000N). The optical properties of Eu doped ZnO films was studied using shimadzuUV-Visible-1700 spectrophotometer. The electrical properties of the undoped and Eu doped ZnO films were determined by Ecopia: HMS-5000 Hall measurement system using the Van der Pauw's method in a magnetic field strength of 0.5 T at room temperature.

2. Experimental Work

Nanostructured Eu doped ZnO thin films were prepared by a spray pyrolysis technique using Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$) as a source of zinc. In a typical experiment; Zinc acetate dihydrate was added to 10 ml of ethanol and 90 ml deionized water and stirred vigorously at room temperature for 45 min. A small amount of acetic acid was added into the solution to avoid the formation of milky precipitate of hydroxides (Swapna et al., 2012). The concentration of europium nitrate was 2 at %. The total concentration of the solution was maintained at 0.1M. The glass substrates were cleaned with detergent solution and deionized water. Ultrasonic cleaning was carried out for 30 min in an ultrasonic bath and then rinsed in acetone for 10 min and finally dried in hot air oven. The nozzle was at a distance of 10 cm from the substrate during deposition and solution flow rate was held constant at 3 ml/min. Air was used as the carrier gas, at the pressure of 2 bar. When aerosol droplets come close to the substrates, a pyrolytic process occurs and high quality Eu doped ZnO films were produced. The deposition of Eu doped ZnO films were carried out at substrate temperature of 623 K with 987 ± 8 nm thickness. Then the films were inserted to a furnace and annealed at 673 K, 723 K for 60 min.

3. Results and discussion

3.1 Structural analysis

The XRD spectra (Fig. 1) of Eu doped ZnO nano thin films deposit on glass substrate reveals the formation of highly preferential c-axis oriented ZnO films. It can be observed from Fig. 1 that the entire films exhibit the

characteristic diffraction peaks of ZnO indicating that the films are in polycrystalline form with wurtzite structure. The preferential or random growth of polycrystalline thin films can be understood by calculating the texture coefficient $TC(hkl)$ for all planes (Swapna et al., 2013). It is clear from the definition that the deviation of texture coefficient from unity implies the film growth occurs in certain preferred orientation. The texture coefficients of the (002) plane of the films are between 2.51 and 2.98. The texture coefficient increases with increase of annealing temperature. This means that the increase in preferred orientation associated with the increased number of grains along that plane.

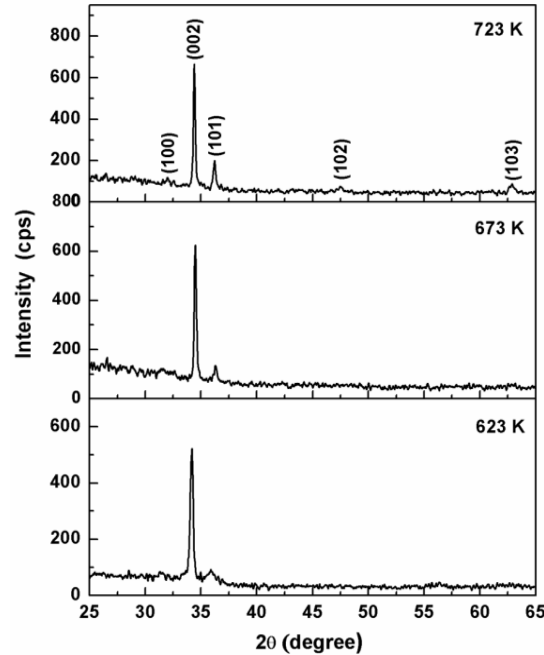


Fig. 1 XRD patterns of Eu doped ZnO films as-prepared at 623 K and annealed at 673 K and 723 K.

The average crystallite size ‘D’ is calculated using the Scherrer’s formula (Swapna et al., 2012).

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the wavelength of CuK_{α} radiation (1.5406 Å), β is the broadening of the diffraction line (FWHM) and θ is the Bragg’s diffraction angle. The average crystallite size of Eu doped ZnO films is 38 nm, 43 nm, and 50 nm, respectively. The crystallite size increases with the increase of annealing temperature. During annealing process the ZnO:Eu films are re-crystallized. The lattice mismatch between ZnO:Eu thin film and substrate can result in varying degrees of strain during the growth process of ZnO thin films. The results (Table 1) show that all fabricated ZnO:Eu thin films present the tensile strain, which derived from lattice mismatch between substrates and ZnO thin films owing to increasing crystalline size, and the strain is decreased as the growth temperature increases (Rao et al., 2011).

Table 1: Calculated Crystallite size, TC and strain values of ZnO:Eu thin films with different annealing temperature

Temperature	Crystallite size (nm)	Texture coefficient (TC)	Strain (%)
As-prepared at 623 K	38	2.51	0.93
Annealed at 673 K	43	2.74	0.31
Annealed at 723 K	50	2.98	0.29

3.2 Surface morphology and Compositional analysis

The surface morphology of as-prepared and annealed Eu doped ZnO thin films are shown in Fig. 2(a) and 2(b). The Eu doped ZnO (ZnO:Eu) films consist of many spherical grains distributed throughout the film surface. Compared with as-prepared ZnO:Eu film, the grain size becomes larger for the annealed ZnO:Eu film. Thus the SEM analysis corroborates the XRD studies. The EDX spectrum of 2 at.% as-prepared Eu doped ZnO thin films is shown in Fig. 3. The EDX analysis show the presence of Zn, O, Eu for the 2 at.% ZnO:Eu films and the chemical compositions of these elements are identified as 42.92, 55.68, and 1.40 at.%, respectively.

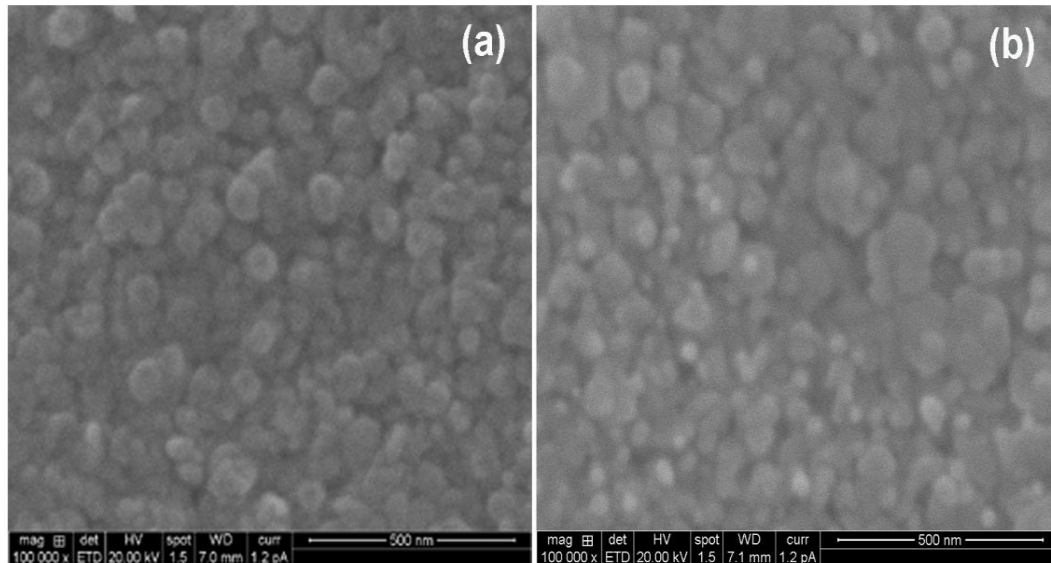


Fig. 2 SEM micrographs of Eu doped ZnO films (a) as-prepared at 623 K and (b) annealed at 723 K.

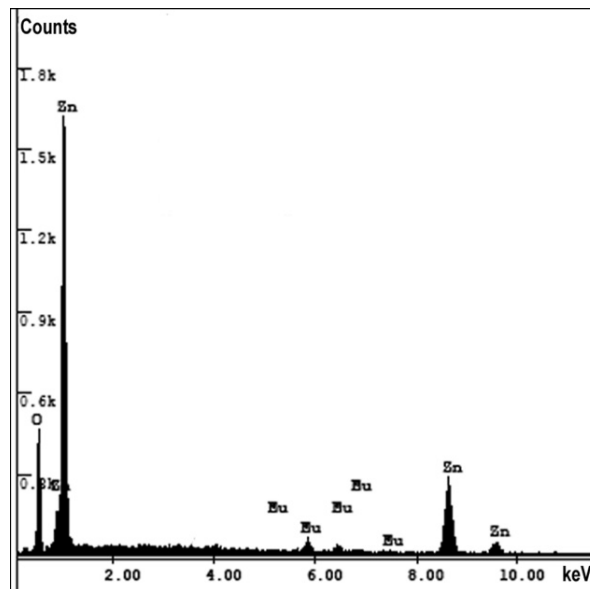


Fig. 3 EDX spectrum of as-prepared Eu doped ZnO thin films at 623 K

3.3 Optical studies

The transmittance and reflectance spectra of Eu doped ZnO thin films in the wavelength range of 300–1100 nm are shown in Fig. 4. All films are highly transparent in the visible wavelength range and sharp ultraviolet absorption edge is observed at approximately 375 nm in the UV region. The annealed ZnO:Eu films show good transmittance of about 94%. While as-prepared ZnO:Eu films exhibit an average transmittance of 90% and an average reflectance of 8% observed in the visible region. The observed increase in the transmittance of annealed ZnO:Eu is due to optical scattering caused by rough surface of the film. This is a very important result since our main goal is to prepare highly transparent and conductive electrodes for device application. In addition, a shift towards the lower energies of the absorption edge with increasing annealing temperature is noticed. The incorporation of Eu is accompanied by a systematic low-energy shift of the band gap indicating the narrowing of the optical band gap. The average optical band gap of the annealed ZnO:Eu films is 3.284 eV.

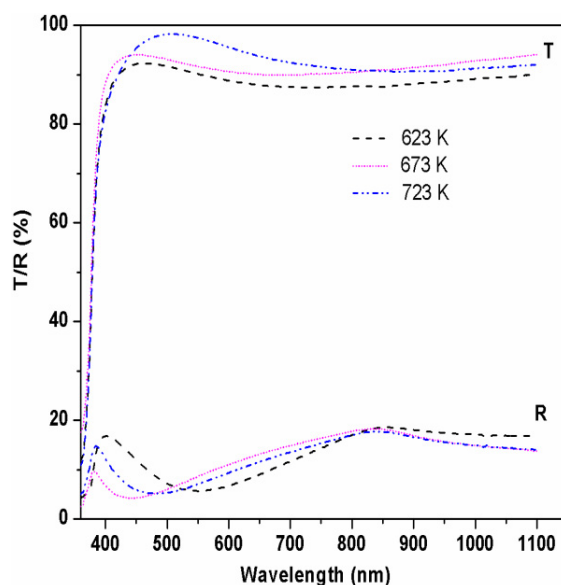


Fig. 4 Optical transmittance and reflectance spectra of as-prepared (623 K) and annealed (673 K and 723 K) Eu doped ZnO thin films.

3.4 Electrical characteristics

The Hall measurements data of the undoped and annealed Eu doped ZnO films made at room temperature in a magnetic field strength of 0.5 T. Table 2 shows the measured carrier concentration, mobility and resistivity of as-prepared and annealed 2 at.% Eu doped ZnO thin films. The Hall measurement data shows that the increase in the carrier concentration of the ZnO films after doping with the trivalent europium ions indicates that divalent zinc ion being replaced by trivalent europium ions. The lower recorded resistivity value is $3.62 \times 10^{-4} \Omega \text{ cm}$ for the sample annealed at temperature of 723 K. The electrical conduction in ZnO is dominated by electrons generated from O^{2-} vacancies and Zn interstitials. However in ZnO:Eu films the conductivity is better comparatively to undoped ZnO films owing to Eu^{3+} ions at substitutional Zn^{2+} sites (Igazaki et al., 1991). When, Eu^{3+} substitutes Zn^{2+} site in the ZnO crystal structure resulting in more free electrons that contribute to the n-type conduction (Kim et al., 2002). The decrease of resistivity with annealing temperature is due to the enhancement of film crystallinity and carrier concentration.

Table 2: Carrier concentration (n), Mobility (μ) and Resistivity (ρ) of the ZnO:Eu thin films with various annealing temperature

Material	Temperature	Carrier concentration (cm^{-3})	Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Resistivity (Ωcm)
Undoped ZnO	As-prepared at 623 K	5.65×10^{15}	0.33	3.33×10^3
Eu doped ZnO	As-prepared at 623 K	5.18×10^{19}	41.1	2.93×10^{-3}
	Annealed at 673 K	2.55×10^{20}	16.4	1.49×10^{-3}
	Annealed at 723 K	5.95×10^{20}	29.0	3.62×10^{-4}

In fact, this is due to the reduction in the scattering of the carriers at the grain boundaries and crystal defects, which increases the carrier concentration (Musatet al., 2004; Xu et al., 2006). For the practical ZnO:Eu thin film application for the transparent electrode in optoelectronic devices, the high transmittance and low sheet resistance are required. In order to estimate the quality of ZnO:Eu thin film, the figure of merit defined by Haacke (1976) is calculated as a criteria for performance of transparent conductive oxides. When annealing temperature is increased from 673 K to 723 K for the ZnO:Eu thin film, the figure of merit increases from 4.18×10^{-2} to $2.01 \times 10^{-1} \Omega^{-1}$. The figure of merit increases by annealing process due to the decrease of sheet resistance as well as the enhancement of transparency.

4. Conclusions

The effect of annealing on structural, electrical, and optical properties of Eu-doped ZnO (ZnO:Eu) thin films prepared by spray pyrolysis method is investigated. ZnO:Eu films are polycrystalline with a preferred (002) orientation. The annealed ZnO:Eu thin films are highly transparent in the visible region (400–700 nm) and have a sharp absorption edge in the ultraviolet region. The increase of annealing temperature increases the crystallite size of the thin film. The presence of Eu in the ZnO thin film is confirmed by EDX analysis. The annealed ZnO:Eu films show good transmittance of about 94% and the average optical band gap of the ZnO:Eu films is 3.284 eV. The electrical conductivity improved with increase of annealing temperature.

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